CUCUMIS MELO RIND AS BIOSORBENT TO REMOVE FE(II) AND MN(II) FROM SYNTHETIC GROUNDWATER SOLUTION

Norzila Othman[a] Syazwani Mohd Asharuddin[b]

Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn,

Jalan Kluang, 86400 Batu Pahat, Johor, Malaysia

[a]norzila@uthm.edu.my [b]hf110212@siswa.uthm.edu.my,

Keywords: *Cucumis melo*. Biosorbent. SEM-EDX. FTIR.

Abstract. *Cucumis melo* rind was evaluated as a new biosorbent for the removal of Fe(II) and Mn(II) from synthetic groundwater solution. The maximum sorption capacity of Fe(II) and Mn(II) was found to be 4.98 mg/g and 1.37 mg/g respectively. Sorption was most efficient at pH 7 and 6.5 for Fe(II) and Mn(II) respectively. The biosorption of both metals increased as the quantity of biosorbent increased. The increase in initial metal concentration was associated with steep increase in biosorption at lower concentrations and progressively reaching towards plateau at higher metal concentration. FTIR demonstrated that hydroxyl and carboxyl groups were involved in the biosorption of the metal ions. The study points to the potential of new use of *Cucumis melo* rind as an effective sorbent for the removal of Fe(II) and Mn(II) from aqueous solution.

Introduction

Cucumis melo (honeydew melon) is among major fruits that are grown worldwide. *Cucumis melo* rind is a by-product of the fruit juice industry and local fruit stalls. Therefore, it is inexpensive biosorbent material. *Cucumis melo* rind is naturally enriched with non-essential amino acid citrulline [1], pectin and α-cellulose to provide the function of rigidity and resistance to tearing [2]. Pectin, cellulose and amino acids containing abundant of carboxyl, hydroxyl and amino groups which has significant capabilities of binding heavy metals from aqueous solution [3].

Due to the techno-economic constraints demonstrated by conventional methods of heavy metals removal in groundwater such as chemical precipitation and activated carbon, efforts are being directed towards searching of efficient and low-cost materials. Agricultural products and it wastes are potentially play a major role in treating metal-laden groundwater. Due to high consumption of honeydew, massive amount of rinds are readily available to be used as biosorbent instead being dumped to mountain of waste and causing environmental problems.

Many fruit waste have been studied for their potential in removing heavy metals in metal-poluted water. These includes mandarin peel [4], papaya wood [5], pomegranate peel [6] and yellow passion fruit shell [7]. To the best of our knowledge, there is no literature describe about the potential of using *Cucumis melo* rind in removing heavy metals from groundwater. The purpose of this work is to investigate the posible use of *Cucumis melo* rind as a biosorbent for the removal of Fe(II) and Mn(II) from synthetic groundwater solutions.

Materials and methods

Preparation of Cucumis melo rind. *Cucumis melo* rind was collected from the local fruit stalls in Batu Pahat, Johor, Malaysia. The rind then washed with distilled water, soaked in 15% Nitric Acid (HNO_3) for 24 hours before soaked in deionized water for another 24 hours to remove Nitric Acid residue on the rind. Biosorbent was oven-dried (60°C) until it reaches constant weight. Dried rind was ground using laboratory ball mill then screened to particle size of >150 µm

Experimental Design. All experiments were conducted using batch method by varying pH, rind dosage, contact time, and initial metal ion concentration. The prepared solution were shaken at 125 rpm. Biosorbent were filtered through 0.45 µm filter paper and kept in airtight container for further analysis using Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF) and Fourier Transform Infrared (FTIR). Finally, the supernatants were kept in airtight plastic bottles and analysed by using AAS. Table 1 shows working range of ferum and mangan.

Table 1: Working range for sorption studies

Parameters	Heavy metals	
	Fe(II)	Mn(II)
pH	5.5, 6.0, 6.5, 7.0	5.5, 6.0, 6.5, 7.0
Biosorbent dosage (g)	0.03, 0.04, 0.05, 0.06, 0.08	0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08
Initial metal concentration (mg/l)	2.0,2.1,2.2,2.3,2.4,2.5	0.5, 0.6, 0.7, 0.8, 1.0
Contact time (min)	5, 10, 15, 20, 25, 30, 45, 60	5, 10, 15, 20, 25, 30, 45, 60

Results and discussion

SEM-EDX analysis. In order to examine the textural structure of biosorbent, SEM micrograph was taken before and after biosorption study onto *Cucumis melo* rind biomass (refer with: Fig. 1(a) before biosorption, (b) after Fe(II) biosorption, (c) after Mn(II) biosorption). SEM micrograph of the unloaded biosorbent indicates rough, irregular and porous structure of surface which indicative of a good characteristics to be employed as a natural adsorbent for metallic ions uptake [7]. Similar structure were observed in watermelon rind [8], yellow-passion fruit shell [7] and pomegranate peel [6]. Many new shiny small particles was observed over the surface of loaded-biosorbent. The EDX analysis done on the unused biosorbent identifies the presence of prominent C and O peaks and did not show the characteristics signal of Fe(II) and Mn(II) (refer with: Fig. 2).

FTIR analysis. The sorption pattern of metals onto plant biomass is attributable to the active groups and chemical bonds present on them [9]. Hence, FTIR spectroscopy was done for preliminary quantitative analysis of major functional groups present in unloaded *Cucumis melo* rind used as metal sorbent in the present study (refer with: Fig. 3). Peaks appearing in the FTIR spectrum of unloaded biosorbent were assigned to various chemical groups and bonds in accordance with their respective wavenumbers (cm^{-1}) as reported in Table 2. FTIR analysis in range of $650 cm^{-1}$ to $4000 cm^{-1}$ shows the presence of characteristic polymeric –OH due to the presence of cellulose and pectin [8][9], carboxylate groups as in cases of glucouronates and hemicellulosics [9]. The -OH, -NH, carbonyl and carboxylic groups are identified as important sorption sites [10].

XRF analysis. The high percentage of SiO_2, CaO, $SO_3$and K_2O, 35.30%, 11.10%, 15.50% and 16.00% respectively together with the presence of Al_2O_3 (4.28%) and MgO (0.88%) confirms the presence of protein and polysaccharides in the biosorbent [12].

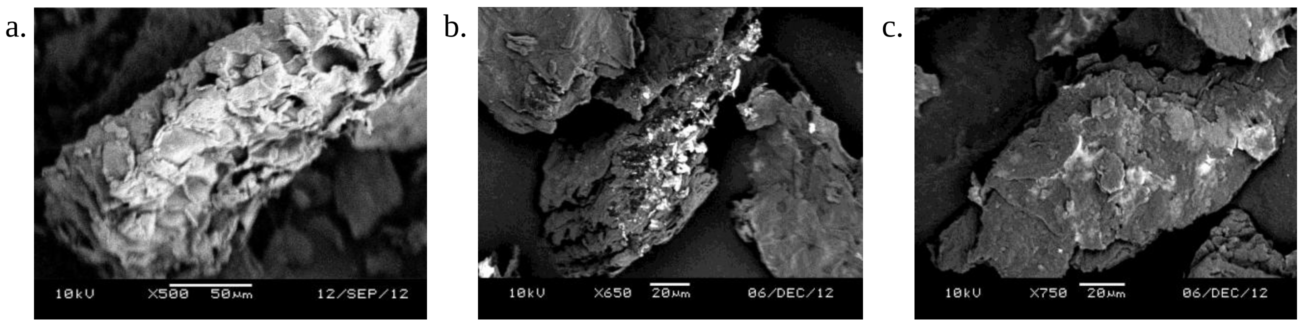

Figure 1: SEM micrographs of *C.melo* biomass (a) before biosorption, (b) after Fe(II) biosorption and (c) after Mn(II) biosorption

a. b. c.

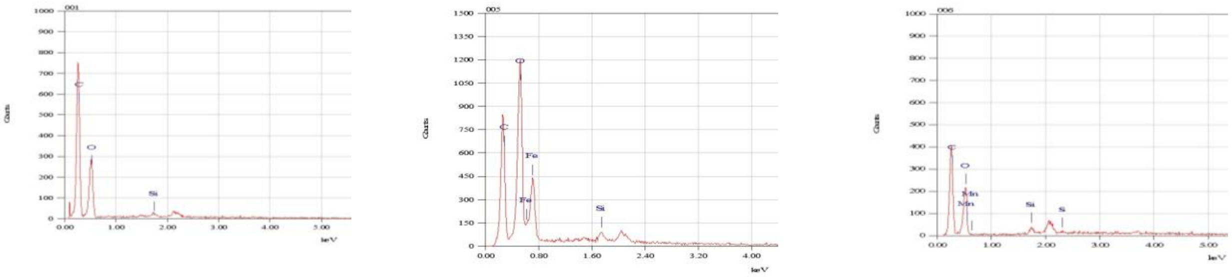

Figure 2: EDX spectra of (a) unloaded biosorbent, (b) Fe-loaded biosorbent, (c) Mn-loaded biosorbent

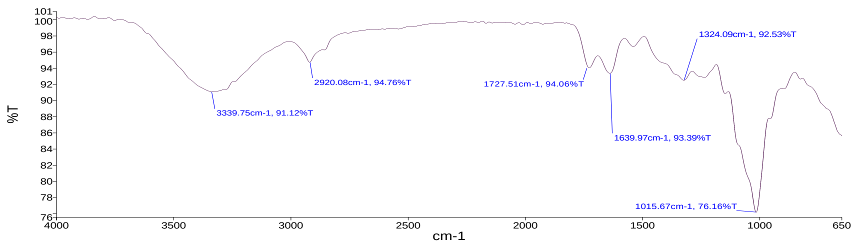

Figure 3: FTIR spectra of the unloaded *Cucumis melo* rind

Table 2: The FTIR spectral characteristics of unloaded *Cucumis melo* rind

Wavelength range [cm^{-1}]	Wavenumber [cm^{-1}]	Identified groups	Reference
3500 – 3200	3339.75	Bonded hydroxyl groups (-OH) and (-NH) groups	[11]
3000 – 2850	2920.08	C-H stretching, -CH, $-CH_2$, $-CH_3$	
1750-1680	1727.51	C=O carbonyl groups	
1640-1500	1629.97	Carboxylate and carboxyl groups	
1375-1300	1324.09	-C-O stretching of -COOH	
1300-1000	1015.67	-C-O or –C-N bonds	

Effects of pH. The extractability of the cations from the aqueous solution is pH dependent. The effects of initial pH for *C.melo* biosorption on Fe(II) and Mn(II) were evaluated within the range of 5.5-7 (refer with: Fig. 4). As can be seen, the highest percentage of removal for Fe(II) and Mn(II) took place at pH 7 and 6.5 respectively. The removal of Mn(II) increased with increasing solution pH from 5.5 to 6.5 and then showed a slightly decreasing trend when pH was higher than optimal pH. The low metal sorption lower ph values may be explained on the basis of active sites protonation, resulting in H^+ and cations competition to occupy the binding sites [13]. When pH increased over 7, the hydrolysis of metallic ions could take place which leading to decrease in biosorption process [4].

Effects of biosorbent dosage. The quantity of *C.melo* rind was varied between 0.01-0.08g to determine the optimum quantity of biomass needed for maximum sorption (refer with: Fig. 5). From 2.5 mg/l Fe(II) ion solution at pH 7, the maximum biosorption within 60 minutes contact time, 95.42% of Fe removal was achieved with 0.04 g *C.melo* rind. While 98.76% of Mn(II) was removed from 0.7 mg/l Mn(II) ion solution at pH 6.5 when contacted with 0.05g of *C.melo* rind within 60 minutes. The percentage of metal removal increases with biosorbent amount reflected that as the biosorbent amount was increased, the active sites become more surplus thus increasing metal uptake [5].

Effects of initial metal concentration. The mechanism of metal uptake is particularly dependent on the initial metal concentration where at low concentration, metals are absorbed by specific site. While increasing metal concentrations causing the specific sites to be saturated and the exchange sites are filled [14]. After the contact period of 60 minutes, the results revealed that percentage of removal decrease with the increase of metals concentration (refer with: Fig. 6). The optimum Fe(II) and Mn(II) concentration were found at 2.2 mg/l and 0.7 mg/l respectively. The result is as expected due to the fact that during initial stages, the active site are abundantly available for metal sorption and later stages, the active sites are gradually decreasing which resulting in decreasing metal removal [5].

Effects of contact time. The removal of Fe(II) and Mn(II) ions increases with time and attains saturation in about 45 minutes (refer with: Fig. 7). Both metals showed a fast rate of sorption during the first 20 minutes of the sorbent-sorbate contact. The percentage of metal removal from solutions of Fe(II) and Mn(II) ions amounted 98.31% and 98.90% respectively at equilibrium time of 45 minutes. The rate of metal removal is higher in the beginning due to larger surface area of biosorbent being available for the adsorption of the metals. Gradual occupancies of active sites in later stage resulting slower rate of metal sorption [5].

Fe(II) and Mn(II) removal under optimum condition. Study was conducted by employing all the optimum values of each parameter examined earlier. Sorption study for Fe(II) was conducted at pH 7 by contacting 0.08g of biosorbent in 100ml of 2.2 mg/l of Fe(II) ion concentration. Whereas for Mn(II), 0.05g *C.melo* rind was contacted with 100 ml of 0.7 mg/l Mn(II) ion concentration at pH 6.5 for 45 minutes. Contact time was set to 45 minutes. The results demonstrated that maximum uptake capacity of 4.98 mg/g and 1.37 mg/g was achieved for Fe(II) and Mn(II) respectively.

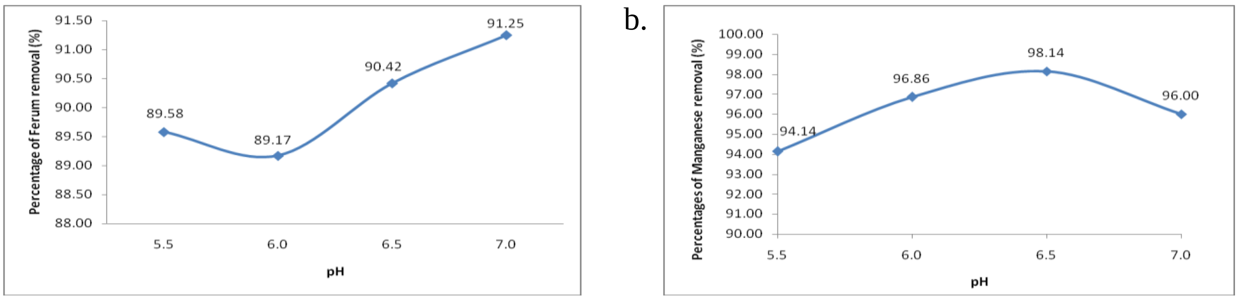

Figure 4: Effect of pH on the biosorption of (a) Fe(II) and (b) Mn(II)

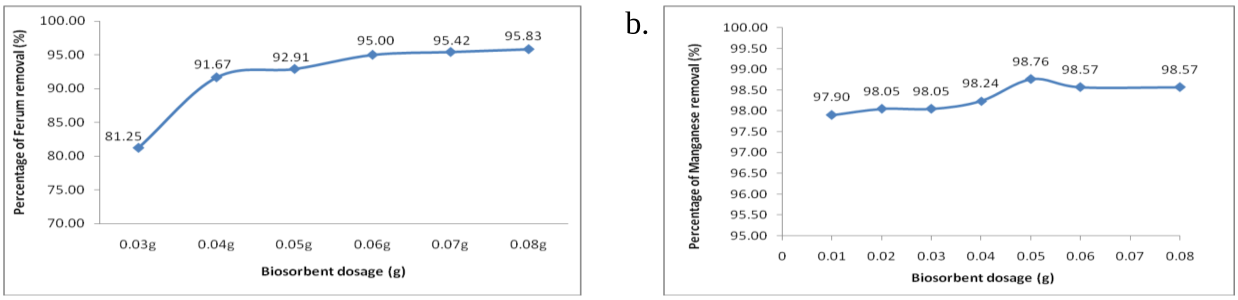

Figure 5: Effect of biosorbent dosage on the biosorption of (a) Fe(II) and (b) Mn(II)

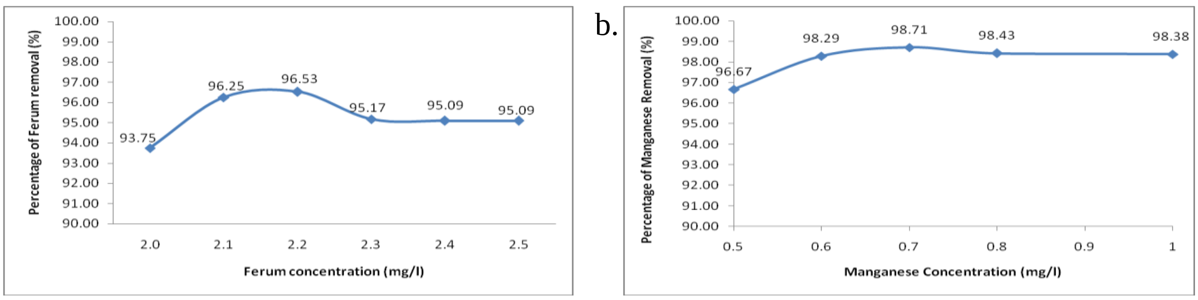

Figure 6: Effect of initial metal concentration on the biosorption of (a) Fe(II) and (b) Mn(II)

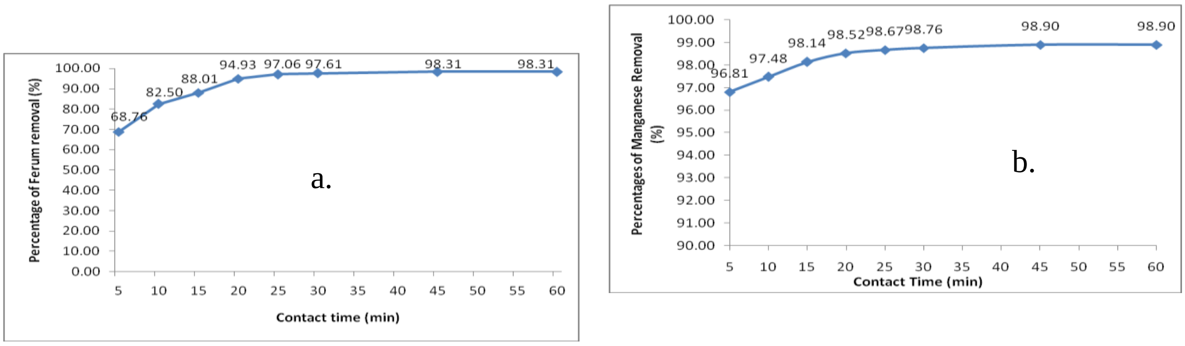

Figure 7: Effect of contact time on the biosorption of (a) Fe(II) and (b) Mn(II)

Conclusion

Cucumis melo rind is potentially to be developed into low-cost and environmental friendly biosorbent for effective elimination of heavy metals in groundwater. The biosorbent was tested without any chemical pretreatment presenting biosorption capacities for Fe(II) and Mn(II) such as 4.98 mg/g and 1.37 mg/g respectively.

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